

## Dyeing Polyester Textile Materials

The invention relates to the use of a transition metal coordination compound for dyeing a fibre fabric or a fibre material comprising polyester fibres for improving the light

5 fastness of the dyeings.

The problem to be solved of the present invention is to improve the fastness to light of dyed polyester material without the need of using modified polyester fiber material.

10 It has been found, that the use of mixtures comprising a transition metal coordination compound for dyeing a fibre fabric or a fibre material comprising polyester fibres improves the light fastness of the dyeings.

15 A further aspect of the present invention relates to the use of at least one transition metal coordination compound for improving the light fastness of dyed polyester material.

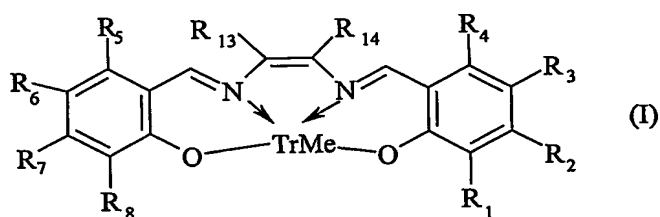
20 By preference, the transition metal coordination compound comprises Ni, Co, Cr or Cu (Nickel, Cobalt, Chromium or Copper). The most preferred transition metal is Nickel (Ni).

25 Therefore this invention relates to the use of at least one transition metal coordination compound for improving the light fastness of dyed polyester material. Preferred transition metal coordination compounds comprise Ni, Co, Cr or Cu (Nickel, Cobalt, Chromium or Copper); more preferred transition metal coordination compounds comprise Nickel (Ni). This invention relates to mixtures of at least one transition metal coordination compound and at least one additional disperse dye.

30 The preferred transition metal coordination compounds are not water soluble e.g. are not acid dyes or direct dyes or basic dyes, which means the preferred transition metal coordination compounds are disperse dyes. Disperse dyes are colorants with low water solubility that, in their disperse colloidal form, are suitable for dyeing and printing hydrophobic fibers and fabrics.

The preferred transition metal coordination compounds in the mixtures according to the invention are compounds with chelating ligands. The preferred transition metal coordination compounds with chelateing ligands comprise at least one chelating ligand which is at least a bidentate ligands. More preferred are transition metal coordination compounds with chelating ligands compriing at least one tridentate ligand. Most preferred transition metal coordination compounds with chelating ligands comprise at least one tertradentate ligand. And the most preferred transition metal coordination compounds have a coordination sphere of at least two nitrogen atoms and at least two oxygen atoms.

The more preferred transition metal coordination compounds have the formula (I)



wherein

TrMe signifies a transition metal and  $R_1$  to  $R_8$  independently from each other signify H, halogen,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  or  $\text{NHCH}_3$  and  $R_{13}$  or  $R_{14}$  independently from each other signify H, halogen or  $-\text{CN}$ , or  $R_{13}$  and  $R_{14}$  form together a ring which is by preference a six membered ring and which may be unsubstituted or may be substituted by halogen,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  or  $\text{NHCH}_3$ .

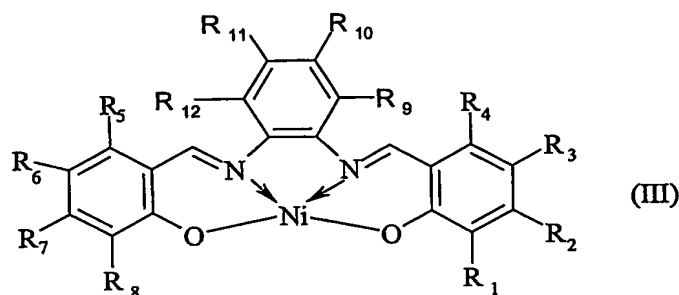
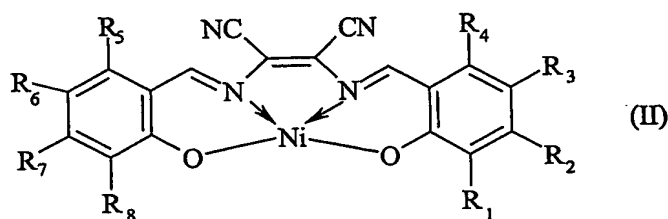
Preferably, transition metal coordination compounds or mixtures of transition metal coordination compounds are used wherein  $R_1$  to  $R_8$  independently from each other signify H,  $-\text{Cl}$ ,  $-\text{COOH}$ , or  $-\text{CN}$ .

In a preferred embodiment the transition metal TrMe is selected from Nickel, Cobalt, Chromium or Copper.

In a more preferred embodiment the transition metal TrMe is Nickel.

For example, the mixture comprises at least one of the transition metal coordination compound according to formula (II) or formula (III)

5



10 wherein  $R_1$  to  $R_{12}$  independently from each other signify H, halogen,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  or  $\text{NHCH}_3$ .

Preferably, transition metal coordination compounds or mixtures of transition metal coordination compounds are used wherein  $R_1 - R_{12}$  independently from each other  
15 signify H,  $-\text{Cl}$ ,  $-\text{COOH}$ , or  $-\text{CN}$ .

The transition metal coordination compound of formula (II), wherein all  $R_1 - R_8$  are H, is known as C.I. Solvent Brown 53 (Polysynthren<sup>®</sup> Braun R, Polysynthren<sup>®</sup> is a registered Trademark of CLARIANT) or a transition metal coordination compound of  
20 formula (III) wherein all  $R_1 - R_{12}$  are H, which is known as C.I. Pigment Orange 70 (Polysynthren<sup>®</sup> Braun 3RL, Polysynthren<sup>®</sup> is a registered Trademark of CLARIANT).

Therefor and the most preferred transition metal coordination compound is either a compound according to formula (II) or formula (III)

The transition metal coordination compounds may be used together with other dyes suitable for dyeing polyester materials. Usually polyester materials are dyed using disperse dyes.

5

In a embodiment the transition metal coordination compounds or the pigments are used in mixtures together with disperse dyes.

10 In the preferred embodiment the transition metal coordination compounds comprises Ni, Co, Cr or Cu (Nickel, Cobalt, Chromium or Copper) and are used in mixtures together with disperse dyes. The most preferred transition metal is Nickel (Ni).

In a more preferred embodiment the transition metal coordination compounds or the pigments have the formula (I) and are used in mixtures together with disperse dyes.

15

In the most preferred embodiment the transition metal coordination compounds or the pigments have the formula (II) or formula (III) and are used in mixtures together with disperse dyes. The most preferred transition metal coordination compounds is either C.I. Solvent Brown 53 or C.I. Pigment Orange 70.

20

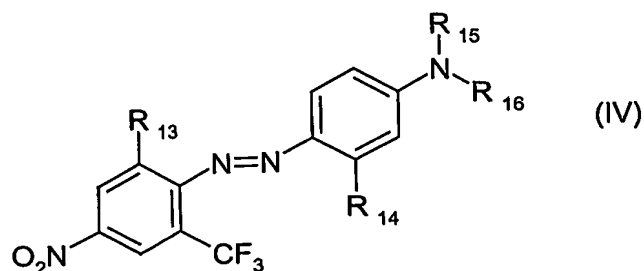
Preferred disperse dyes are for example at least one of the following disperse dyes: C.I. Disperse Yellow 42, C.I. Disperse Yellow 72, C.I. Disperse Yellow 86, C.I. Disperse Yellow 54, C.I. Disperse Yellow 64, C.I. Solvent Yellow 163, C.I. Disperse Red 60, C.I. Disperse Red 86, C.I. Disperse Red 91, C.I. Disperse Red 167, C.I. Disperse Red 167.1, C.I. Disperse Red 202, C.I. Disperse Red 302, C.I. Disperse Red 273, C.I.

25

Disperse Red 279, C.I. Disperse Red 271, C.I. Solvent Red 135, C.I. Disperse Violet 27, C.I. Disperse Violet 57, C.I. Disperse Blue 56, C.I. Disperse Blue 77, C.I. Disperse Blue 54, C.I. Disperse Blue 27, C.I. Disperse Blue 55, C.I. Disperse Blue 60, C.I. Disperse Blue 87, C.I. Disperse Orange 30, C.I. Disperse Orange 41, C.I. Disperse Orange 29,

30

structures according to formula (IV)



wherein

R<sub>13</sub> signifies -Br, -Cl, or -CN;

R<sub>14</sub> signifies -H, -CH<sub>3</sub>, -NHCOCH<sub>3</sub>;

5 R<sub>15</sub> signifies a unsubstituted ethyl group or ethyl group  
which is substituted by -CN, -acyloxy;

R<sub>16</sub> signifies a unsubstituted ethyl group or ethyl group  
which is substituted by -CN, -acyloxy;

10 or mixtures thereof.

Dyes according to the formula (IV) are known for example from EP1085055 A1,  
CH468444, US2941992, US3407189, FR1291988, US2891942, DE2364205 and  
JP49030417 A. Preferred examples are shown in EP1085055 A1 on page 2, line 37 to  
15 page 4, line 23 and in the examples 1 to 20 of EP1085055 A1.

A further aspect of the present invention is a mixture of at least one transition metal  
coordination compound and at least one disperse dye. By preference the at least one  
transition metal coordination compound comprises Ni, Co, Cr or Cu (Nickel, Cobalt,  
20 Chromium or Copper). The most preferred transition metal is Nickel (Ni).

The preferred transition metal coordination compounds in the mixtures according to the  
invention are not water soluble e.g. are not acid dyes or direct dyes or basic dyes, which  
means the preferred transition metal coordination compounds are disperse dyes

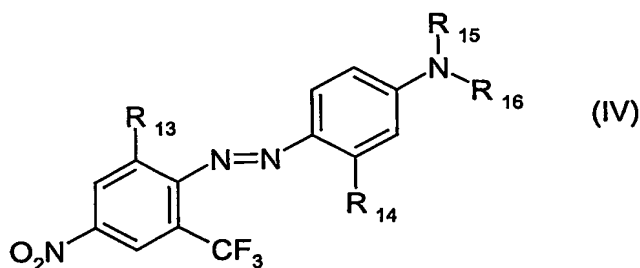
25

The preferred transition metal coordination compounds in the mixtures according to the  
invention are compounds with chelating ligands. The preferred transition metal  
coordination compounds with chelating ligands comprise at least one chelating ligand

which is at least a bidentate ligand. More preferred are transition metal coordination compounds with chelating ligands comprising at least one tridentate ligand. Most preferred transition metal coordination compounds with chelating ligands comprise at least one tertridentate ligand. And the most preferred transition metal coordination compounds have a coordination sphere of at least two nitrogen atoms and at least two oxygen atoms.

In the most preferred embodiment in transition metal coordination compound the transition metal is of formula (I) and preferably the transition metal is Nickel. In a more preferred embodiment the Ni-compound is of formula (II) or formula (III).

The disperse dyes preferably used in the mixtures according to the invention are at least one of the following disperse dyes: C.I. Disperse Yellow 42, C.I. Disperse Yellow 72, C.I. Disperse Yellow 86, C.I. Disperse Yellow 54, C.I. Disperse Yellow 64, C.I. Solvent Yellow 163, C.I. Disperse Red 60, C.I. Disperse Red 86, C.I. Disperse Red 91, C.I. Disperse Red 167, C.I. Disperse Red 167.1, C.I. Disperse Red 202, C.I. Disperse Red 302, C.I. Disperse Red 273, C.I. Disperse Red 279, C.I. Disperse Red 271, C.I. Solvent Red 135, C.I. Disperse Violet 27, C.I. Disperse Violet 57, C.I. Disperse Blue 56, C.I. Disperse Blue 77, C.I. Disperse Blue 54, C.I. Disperse Blue 27, C.I. Disperse Blue 55, C.I. Disperse Blue 60, C.I. Disperse Blue 87, C.I. Disperse Orange 30, C.I. Disperse Orange 41, C.I. Disperse Orange 29, structures according to formula (IV)



wherein

- R<sub>13</sub> signifies -Br, -Cl, or -CN;
- R<sub>14</sub> signifies -H, -CH<sub>3</sub>, -NHCOCH<sub>3</sub>;
- R<sub>15</sub> signifies a unsubstituted ethyl group or ethyl group which is substituted by -CN, -acyloxy;

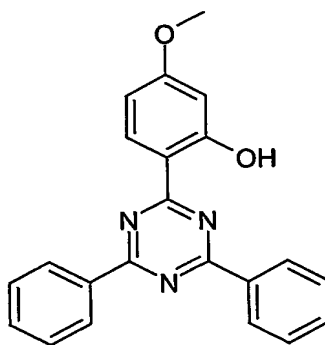
R<sub>16</sub> signifies a unsubstituted ethyl group or ethyl group  
which is substituted by -CN, -acyloxy;

or mixtures thereof.

5

The transition metal coordination compounds can be used according to the invention in any effective ratio with disperse dyes. For example the mixture comprises 2% to 99% of the transition metal coordination compounds, preferably from 50% to 97%.

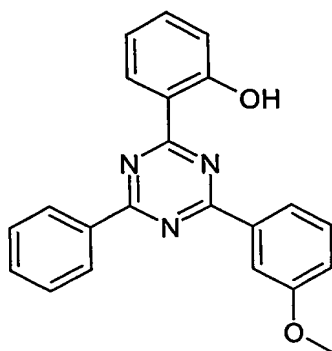
- 10 The transition metal coordination compounds may be used according to the invention together with any UV-absorber. Preferred UV-absorbers are derivatives of 2-hydroxybenzophenones, derivatives of 2-hydroxyphenylbenzotriazoles, derivatives of oxalanilides, derivatives of 2-hydroxyphenyltriazines, derivatives of cinnamates, derivatives of salicylates, derivatives of benzoxazine-4-ones, derivatives of 4,6-diacyl-  
15 resorcinols, or derivatives of formamidines. More preferred UV-absorbers have the formula



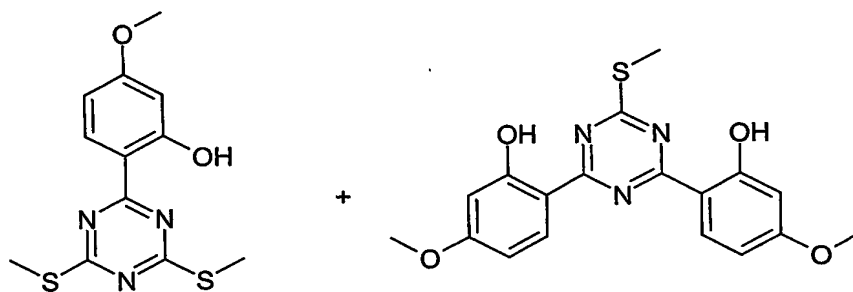
A-1

20

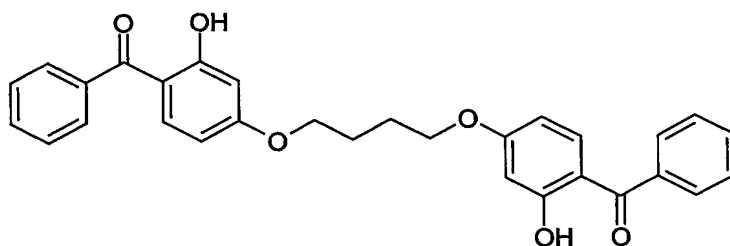
8



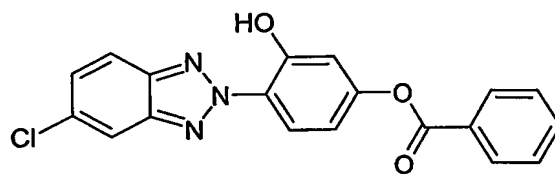
A-2



Mixture A-3



A-4

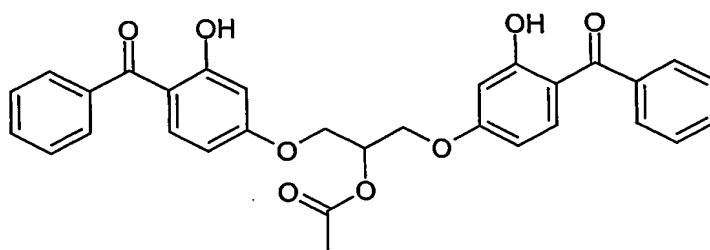


A-5

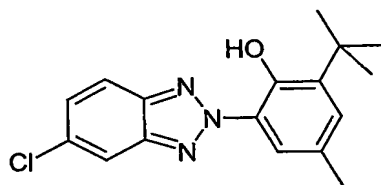
5

10

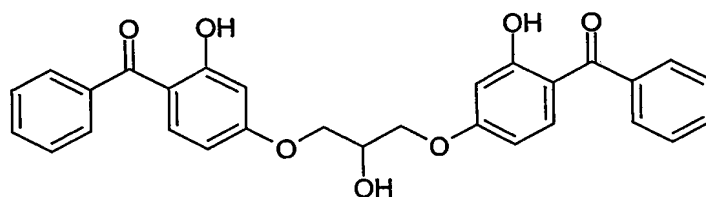




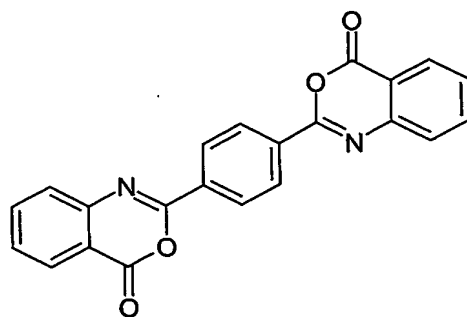
A-6



A-7



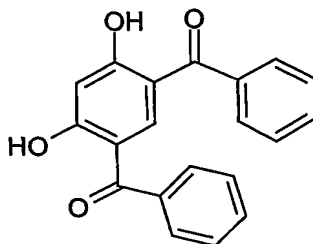
A-8



A-9

5

10



A-10

5 According to the invention, the pigments of formula (I) are used for dyeing and printing semisynthetic and, preferably, synthetic hydrophobic fiber materials, especially textile materials. According to the invention, the pigments of formula (II) or formula (III) as well as mixtures comprising the pigments of formula (II) or formula (III) are used for dyeing and printing semisynthetic and, preferably, synthetic hydrophobic fiber materials, especially textile materials. Textile materials consisting of blended fabrics containing such semisynthetic hydrophobic fiber materials can also be dyed or printed by means of the dyes of this invention.

15 Suitable semisynthetic textile materials are mainly cellulose-2½ acetate, cellulose triacetate polyamides and high molecular weight polyesters as well as mixtures thereof with cellulose.

20 Synthetic hydrophobic textile materials consist mainly of linear aromatic polyester, for example of those consisting of terephthalic acid and glycols, in particular ethylene glycol or condensate of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane; of polycarbonates, e.g. those consisting of alpha,alpha-dimethyl-4,4'-dihydroxydiphenylmethane and phosgene, and of fibers based on polyvinyl chloride and polyamide.

25 The hydrophobic synthetic materials can be in the form of sheet-like or thread-like structures, and can be processed, for example, to yarns or woven, knitted or looped textile fabrics. The mixtures according to the invention are also suitable for dyeing hydrophobic synthetic material in the form of micro fibers.

Dyeing can be carried out by known methods. Additives usual for dyeing with disperse dyes can be added to the bath (e.g. dispersing agents, preferably anionic dispersants, such as aromatic sulfonic acid/formaldehyde condensates, sulfonated creosol oil/-formaldehyde condensates, lignin sulfonates or copolymers of acrylic acid derivatives, preferably aromatic sulfonic acid/formaldehyde condensate or lignin sulfonated, or nonionic dispersants based on polyalkylene oxides obtainable, for examples, by poly-addition reaction from ethylene oxide or propylene oxide. Further suitable dispersants are listed in US 4,895,981 or US 5,910,624.

- 10 The transition metal coordination compounds according to formula (I) are suitable for dyeing by the thermosol process, for the exhaust and continuous process and for printing as for modern imaging processes, e.g. thermo-transfer printing or ink-jet printing.

- 15 Preferably dyeing with the disperse dyes (e.g. for the polyester fibres of a mixed fibre substrate) is performed at pH of 3-9 more preferably 4-6, most preferably 4-5.5 and at a temperature of 125 DEG-135 DEG C. for 15-45 minutes.

After dyeing in a process according to the invention, conventional washing and drying steps may be employed.

20

A further aspect of the present invention relates to the fiber material and textile material dyed with a dye mixture comprising a transition metal coordination compound according to formula (I)

- 25 The textile material dyed using a mixture comprising a transition metal coordination compound and a disperse dye provides dyed textile materials having good light fastness. Since the the textiles have light fastnesses under warm and humid conditions like they occur in closed cars or motor vehicles, this textile material dyed according to the invention is suitable for example as upholstery material in car manufacturing or any other application where improved light fastness is desired for example for an article of clothing or for a sun blind or textiles for outdoor furnitures.
- 30

## **APPLICATION EXAMPLE**

17.5 parts of the pigment and disperse dye mixture (96% C.I. Solvent Brown 53 and 4% C.I. Disperse Red 86; this is the dye mixture from example 23a of table 1) with 32.5 parts of a commercial dispersing agent based on lignin sulphonates, and pulverized to a powder. 1.2 parts of this dye preparation are added to 2000 parts of demineralized water of 70°C, which contains 40 parts of ammonium sulfate; the pH value of the dye bath is set at 5 with 85% formic acid. 100 parts of washed polyester fiber fabric are placed in this dye bath, the container is closed, heated to 130°C over the course of 20 minutes, and dyeing continues for a further 60 minutes at this temperature. After cooling, the polyester fiber fabric is removed from the dye bath, rinsed, soaped and cleansed by reduction with sodium hydrosulphite in the usual way. After thermo-fixation (180°C, 30 min), a brownish pink dyeing is obtained with very good all-round fastness, especially fastness to light and sublimation, in particular excellent wet fastness.

15

The dyed swatches were exposed to light by the fakra standard test. FAKRA is a test according to ISO 105/B02: Exposure in Xenotest 450 equipped with a Xenon arc source; black standard temperature 45 °C, relative humidity  $45 \pm 5$  %. The number of cycles is indicated in tables as times this cycle: 2 cycles fakra means two cycles of this Fakra test; in DIN 75202/H: one cycle FAKRA is 54 hours exposure.

20

Afterwards the adjacent fabrics are assessed by the Grey Scale Change ISO A03. This 5-step Grey Scale consists of 5 pairs of swatches of grey and white cloth which illustrate the perceived color differences corresponding to fastness ratings 5, 4-5, 4, etc. The fastness rating is that number of the Grey Scale which has a perceived color difference equal in magnitude to the perceived color difference between the original adjacent fabric and the treated adjacent fabric. An improvement of a value by 1 signifies an improvement of 20%

25

30 The results are summarized in table 1, table 2, table 3 and table 4.

In tables the amount of the dyes is given in percent of the polyester fiber material dyed in the respective dying bath. The ratio of the different components is also given as

percentage of the total amount of dyestuff used in the dying bath. Eventually an additional UV Absorber is applied, for example a UV-absorber of formula A-8 used in weight-% of dyed PES fiber material. The amount of the UV absorber is given in percent of the weight of the fabric treated. The results of the fakra test is given as explained above

**Table 1**

Dye	23a	24a	25a	26a	27a	28a
C.I. Solvent Yellow 163	0	0	9	0	0	33
C.I. Solvent Brown 53	96	96	90.9	83	83	67
C.I. Disperse Red 86	4	0	0	17	0.0	0
C.I. Disperse Blue 77	0	4	0	0	17	0
UV-absorber of formula A-8 used in weight-% of dyed PES fiber material	2	2	2	2	2	2
2 cycles Fakra	4.5	4.6	4.7	4.8	4.9	4.9
4 cycles Fakra	4.3	4.3	4.5	4.6	4.7	4.7
6 cycles Fakra	4.1	4.2	4.5	4.5	4.6	4.6
8 cycles Fakra	4.0	4.1	4.3	4.4	4.5	4.7
10 cycles Fakra	3.7	3.9	4.2	4.1	4.3	4.6
dystuff used in weight-% of dyed PES fiber material	0.520	0.520	0.550	0.120	0.120	0.150

**Table 2**

Dye	29a	30a	31a	32a	33a	34a
C.I. Solvent Yellow 163	0	0	9	0	0	33
C.I. Pigment Orange 70	96	96	91	83	83	67
C.I. Disperse Red 86	4	0	0	17	0	0
C.I. Disperse Blue 77	0	4	0	0	17	0
UV-absorber of formula A-8 used in weight-% of dyed PES fiber material	2	2	2	2	2	2
2 cycles Fakra	4.4	4.5	4.6	4.8	4.8	4.8
4 cycles Fakra	4.1	4.2	4.3	4.4	4.6	4.7
6 cycles Fakra	3.8	3.9	4.1	4.2	4.3	4.5
8 cycles Fakra	3.6	3.8	4.1	4.0	4.3	4.4
10 cycles Fakra	3.4	3.6	3.8	3.8	4.2	4.2
dystuff used in weight-% of dyed PES fiber material	0.401	0.409	0.403	0.108	0.485	0.496

**Table 3 (The examples 1a, 2a are 1b are comparative examples.)**

In table 3 green shades are realized and example 1a (comparative) has the same shade as example 3a

5

dye	1a	2a	3a
C.I. Disperse Yellow 42	57	0	0
C.I. Solvent Yellow 163	0	45	22
Mixture of C.I. Disperse Red 86 and C.I. Solvent Red 135	0	24	12
C.I. Disperse Red 86	21	0	0
C.I. Solvent Brown 53	0	0	47
C.I. Disperse Blue 77	15	31	0
C.I. Disperse Blue 60	7	0	18
UV-absorber of formula A-8 used in weight-% of dyed PES fiber material	2	2	2
7 cycles Fakra	2.7	2.5	3.5
dystuff used in weight-% of dyed PES fiber material	0.666	0.510	0.403

**Table 4 (The examples 2b, 4b, and 5b are comparative examples)**

In table 4 dark green shades are realized. The examples 1a, 2a, 1b, 2b, 4b, and 5b are comparative examples.

5

dye	1b	2b	3b	4b	5b
C.I. Disperse Yellow 42	49	0	0	44	0
C.I. Solvent Yellow 163	0	33	0	0	30
Mixture of C.I. Disperse Red 86 and C.I. Solvent Red 135	0	24	2	0	24
C.I. Disperse Red 86	25	0	0	25	0
C.I. Solvent Brown 53	0	0	13	0	0
C.I. Pigment Orange 70	0	0	53	0	0
C.I. Disperse Blue 77	27	43	31	31	45
C.I. Disperse Blue 60	8	0	0	9	0
UV-absorber of formula A-8 used in weight-% of dyed PES fiber material	2	2	2	2	2
7 cycles Fakra	2.3	2.7	3.5	2.7	2.5
dystuff used in weight-% of dyed PES fiber material	1.230	0.880	1.051	1.280	0.990